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Summary

The National Bureau of Standards (NBS) Synchrotron Ultraviolet Radiation Facility (SURF-II) is used in conjunction with a high flux normal incidence monochromator for angle resolved wavelength dependent photoelectron studies. The recent work has concentrated on studies of the effect of shape resonances on molecular vibrational intensity distributions as well as the effects of autoionization upon the vibrational intensity distributions over narrow wavelength regions. Results for CO, N₂, Ar and Xe will be discussed.

Introduction and Experimental Design

A companion paper¹ at this meeting describes the NBS-SURF-II storage ring facility in some detail, however, a few observations are relevant for discussion here. The beam size is small, height about .1mm and width 1.5 mm. This small size allows for direct use of the beam as a source for a focussing monochromator without an entrance slit. The storage ring energy of about 250 MeV provides usable photon fluxes down to about 50Å. There is no radiation hazard in the vicinity of the ring after injection. The monochromator and experiments can be placed near the source so as to optimize the illumination of the appropriate optics for high flux monochromators. These features have been exploited in a 2 meter normal incidence device which is used for the experiments described here.² A rotating 2" mean radius hemispherical

electron spectrometer has been constructed and attached to the monochromator in a magnetically shielded chamber. The electron spectrometer has been discussed in detail in the literature.³ The entire device is shown in Figure 1. The electron spectrometer rotates so as to sample electrons as a function of angle with respect to the polarization vector of the light. The light has measured polarization of 70-75% over the wavelength covered in the experiments reported here.

The entire apparatus is under the control of a CAMAC based LSI-11 computer system. The light intensity, electron counts and appropriate voltages are digitally recorded on floppy disks and the sequence of controlled experimental parameters is automated. The data is reduced and the appropriate parameters are determined by analysis using the LSI-11 computer. The typical measurement will consist of accumulating the photoelectron spectra over an established energy range at a given wavelength as a function of angle. Typically three angular positions are used for redundant checks. At a given photon energy the differential cross section for the photoionization process can be expressed in the following form:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta/4 [3P \cos(\theta) + 1]]$$

where σ is the total cross section, β the asymmetry parameter, P the polarization of the light, and θ the angle of ejection of the photoelectron with respect to the electric field vector of the light. From the known polarization and integrated count at

HIGH THROUGHPUT NORMAL INCIDENCE MONOCHROMATOR AT SURF — II
COUPLED TO ELECTRON SPECTROMETER

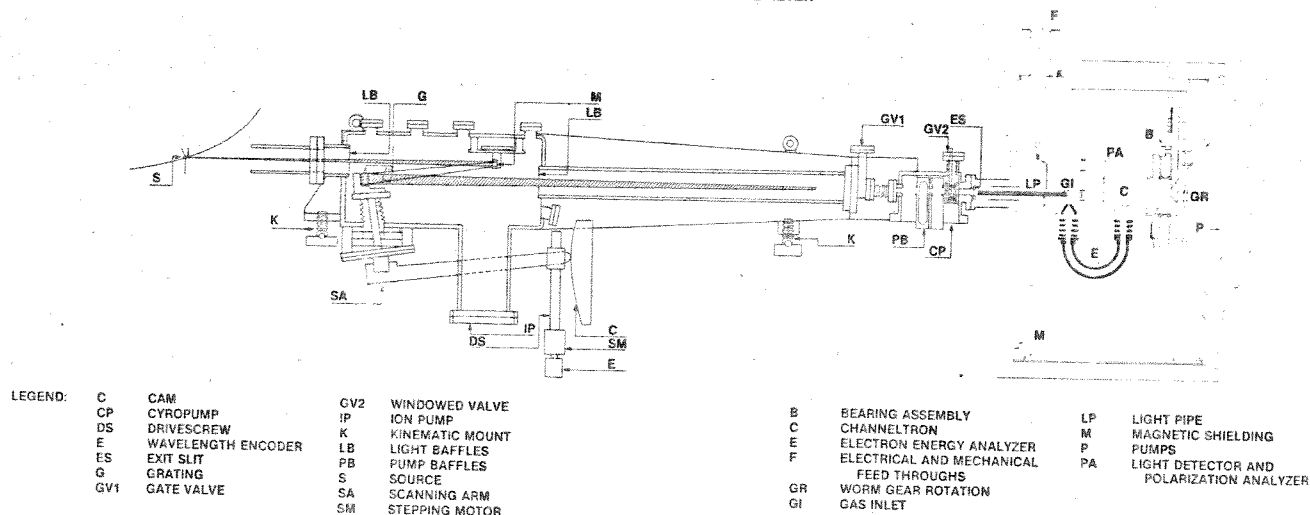


Figure 1. Diagram of high flux 2-meter normal incidence monochromator at NBS-SURF-II. For graphical reasons the storage ring source (S) is shown at right angles to its true position.

three different angles one can determine the value of β and the relative cross section.

Atoms

The asymmetry parameters, β , and the branching ratio's of the $3s3p^6 4p^1 P_1^o$ resonance in Ar and the $5s5p^6 6p^1 P_1^o$ resonance in Xe have been measured. The results are shown in Figures 2 and 3⁴. The figures illustrate the branching ratios $\sigma(^2P_{3/2}): \sigma(^2P_{1/2})$, for both atoms. In Ar the result is essentially a constant value while in Xe the branching ratio departs from a constant value and shows structure. Although the value does not rise as high as that suggested by Jemey et al.⁵, it does rise above the statistical ratio of 2. The variation in β for Ar through the window resonance is the same for both components while for Xe the variation is somewhat different.

Considerable work has been done on the Stark effect in gases using the high flux 2 meter instrument⁶. Measurements have been reported on Xe, Ar, and Kr and an extensive survey has been carried out on diatomic molecules.

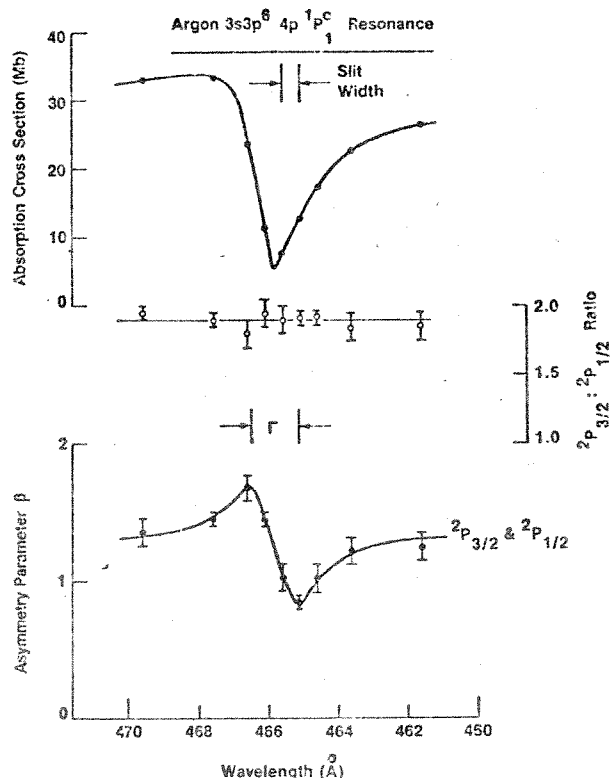


Figure 2. Branching ratio's and asymmetry parameter β , for Ar in the $3s3p^6 4p^1 P_1^o$ window resonance. The photoelectron intensity has been normalized at the known cross section.

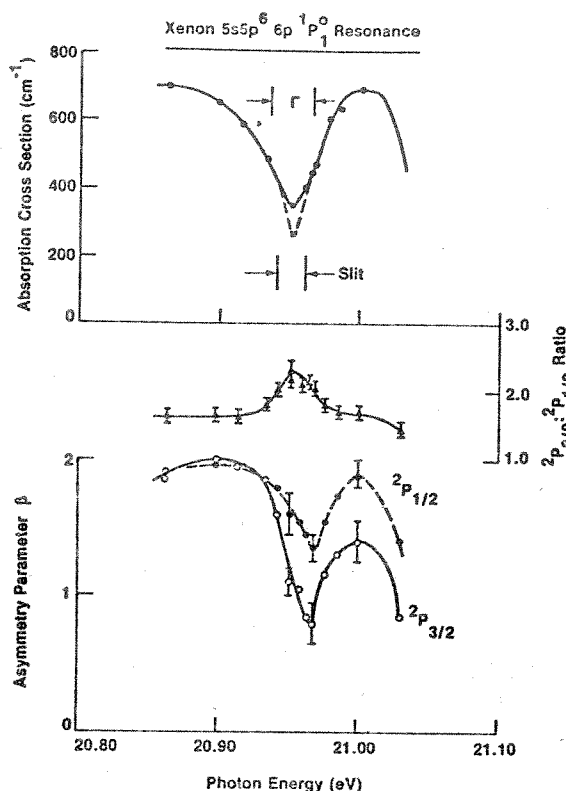


Figure 3. Branching ratio's and asymmetry parameter β , for Xe in the $5s5p^6 6p^1 P_1^o$ window resonance region. The total cross section has been normalized to known values. The dashed curved is a higher resolution piece of data convoluted with a 15Å FWHM gaussian to simulate our resolution.

Molecules

Recent theoretical work by Dehmer, Dill and Wallace⁷ has predicted a pronounced intensity variation for various vibrational transitions in molecular photoionization due to a shape resonance. The shape resonance is essentially due to a centrifugal barrier which forms quasi-bound states. The lifetime and hence width of these states are a strong function of the internuclear distance and are as a consequence reflected in changes in the vibrational intensities.

A shape resonance exists in the 5σ photoionization channel of CO.^{8,9} The branching ratio's for transitions

to various vibrational levels of CO in the 19 to 27eV range shown in Figure 4. The vibrational intensity distribution differs significantly from that predicted by Franck-Condon factors which for the case of $V=1/V=0$ is about 3.8%. The $V=2/V=0$ and $V=3/V=0$ are predicted by Franck-Condon factors to be diminishingly small. The asymmetry parameters for the same energy region is shown in Figure 5. The higher vibrational levels undergo a significant fluctuation in β in the region above 20eV. This is a manifestation of the shape resonance effect. The fluctuations below 20eV are probably due to autoionization.

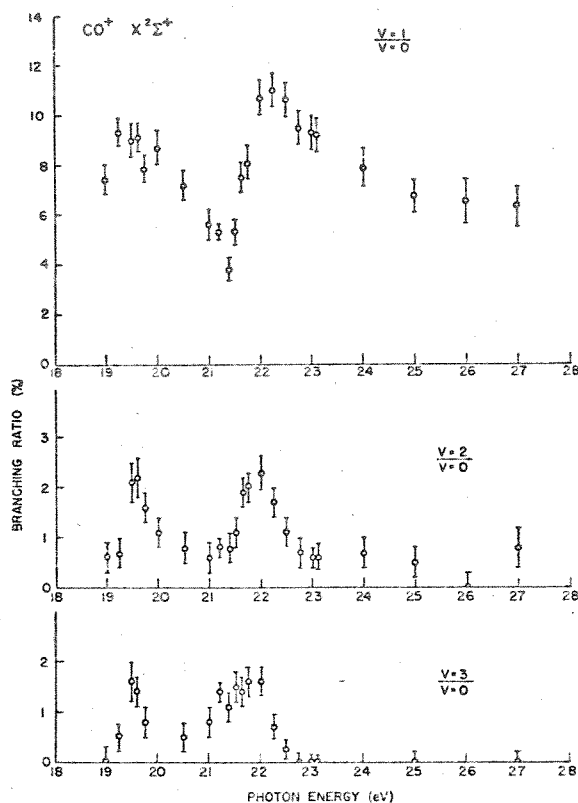


Figure 4. Branching ratio's for CO photoionization in the 18 to 28eV region.

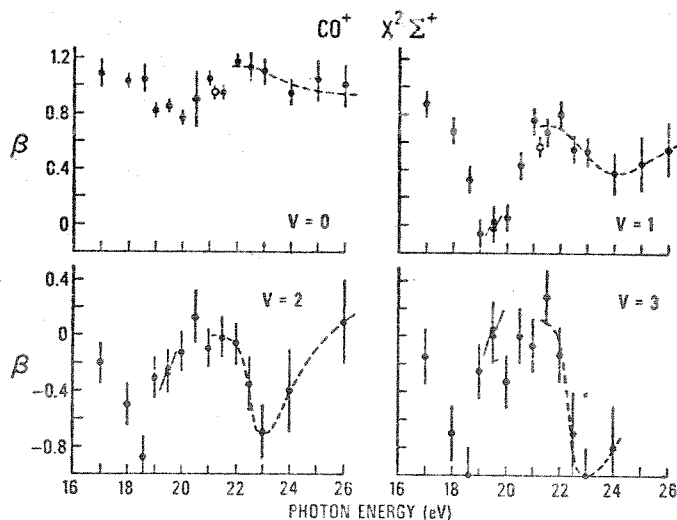


Figure 5. Asymmetry parameter for CO in the 18 to 28eV region.

Figure 6 shows the branching ratio between the first two vibrational levels, $V=1$ to $V=0$, of the $X^2\Sigma^+$ state of molecular nitrogen in the region of a predicted shape resonance.^{7,10} The features of the shape resonance extend over a large (~30eV) energy range and are in general agreement with the calculation shown by the solid line. The horizontal dashed line represents the Franck-Condon factor for this transition.¹¹ The lack of an exact agreement between theory and experiment is probable due to the use of a simple one electron model and the neglect of correlation effects. The major point, however, is

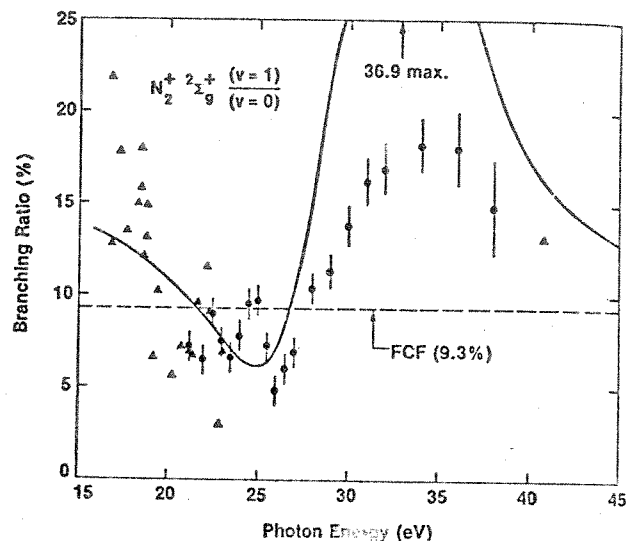


Figure 6. Branching ratio's for $V=0$ to $V=1$ vibrational levels in the photoionization of N_2 in the 15 to 45eV region.

that this work shows for the first time the relationship between the shape resonance and vibrational intensity distributions with a reasonably good agreement between theory and experiment.

Recently we have completed studies on isolated autoionizing states in molecular CO, O₂ and N₂.^{12,13,14} The molecular autoionizing state can interact with the vibrational and rotational modes of the final ionic states yielding a manifold of ionic excitations different from that obtained by direct ionization. The effects of the interaction are complicated and have only recently been addressed by detailed theory for the case of H₂.¹⁵ The effect of autoionization is to provide a temporary state of the system which is short lived and which couples to various states of the ion and free electron. The presence of this temporary autoionizing state disturbs the Franck-Condon density and the angular distribution of the photoelectrons. This can be seen in Figures 7 and 8. Figure 7 shows a well resolved branching ratio measurement of N₂ between 710Å and 728Å. The molecule's ion is left in the $X^2\Sigma^+$ ground electronic state with vibrational excitation as shown, ($V=0,1,2,3$). There is a window resonance

at 715.5Å and an absorption resonance at 723.3Å which are members of an autoionizing series converging to the $V=0$ level of the $N_2^+ B^2\Sigma_g^+$ state. The branching ratios show significant fluctuations going through these resonances. The asymmetry parameters shown in Figures 8 also undergo significant variations in magnitude. It is also interesting to note the small variation in the branching ratios at 720Å, midway between the position of the known spectroscopic levels. The origin of this is uncertain but perhaps represents another state as yet undetected spectroscopically.

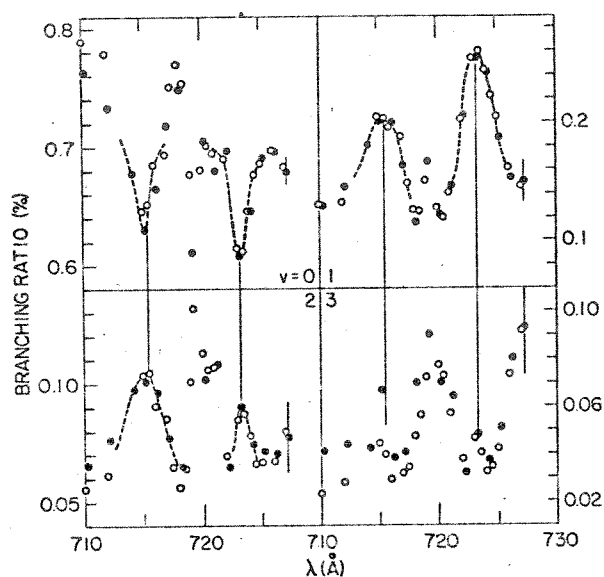


Figure 7. Branching ratio's for the photoionization of N_2 in the 710Å to 730Å region. The first four ($v=0,1,2,3$) vibrational levels of the ground state of N_2^+ are shown.

Conclusions

Triply differential photoelectron studies using continuous wavelength capability such as provided at SURF-II has provided information on resonance processes in ionization. This promises to be an important tool in studying atomic and molecular photoionization dynamics.

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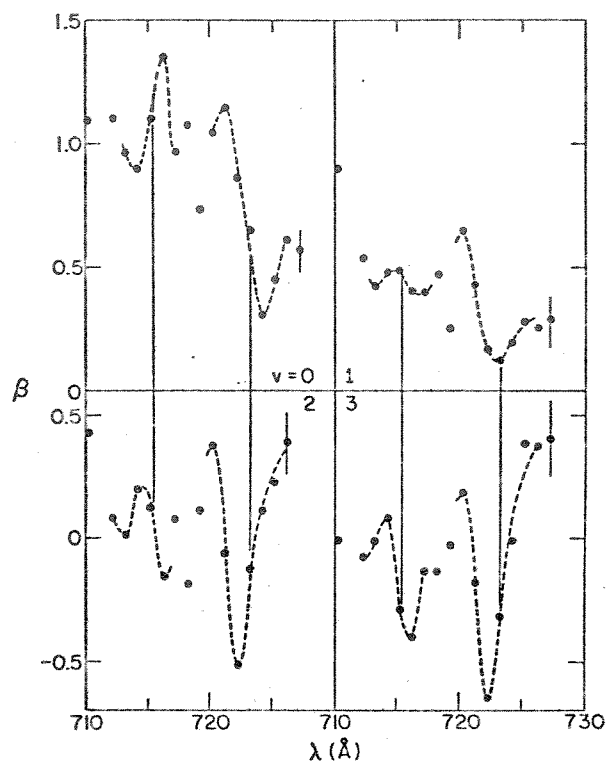


Figure 8. Asymmetry parameter for the first four vibrational levels of the ground state of N_2 over the wavelength region of 710Å to 730Å.

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